The reaction between CO2 and diethanolamine at 298 K

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Table 1. Experimental (Sioda, 1970), and calculated [eq. (5)] total mass transfer rates (I_T) to a cylindrical wire electrode placed diametrically in a flow tube

Re'	I_T (exp.)† ($\times 10^{10}$/mol/s)	$\bar{u}$ (cm/s)	Int	I_T (calc.) ($\times 10^{10}$/mol/s)
0.0690	1.7781	0.0290	0.5146	1.1753
0.0786	1.8688	0.0331	0.5196	1.2402
0.0968	1.9727	0.0407	0.5285	1.3514
0.1379	2.1891	0.0581	0.5451	1.5694
0.2190	2.5094	0.0922	0.5704	1.9156
0.3460	2.9172	0.1457	0.6010	2.3509
0.5226	3.2371	0.2200	0.6353	2.8510
0.7840	3.8253	0.3300	0.6787	3.4865
0.8735	3.9688	0.3677	0.6925	3.6880
1.5159	4.7246	0.6381	0.7884	5.0457
1.7651	4.9450	0.7431	0.8272	5.5698
2.2030	5.2658	0.9274	0.9030	6.5462

† Flow tube diameter = 5 mm, platinum wire diameter = 0.2 mm, electrolyte = 4 mM $K_3Fe(CN)_6$ in 1 M KCl (aqueous); temperature = 25°C, kinematic viscosity = 8.42 cSt, diffusivity = 0.73×10^{-5} cm^2/s [after Konopka and McDuffie (1970)].

D diffusivity, cm^2/s
I mass transfer rate of diffusing substrate for constant bulk flow velocity v_o, mol/s
Int value of integral of eq. (6)
l length of cylinder (wire), cm
r radial coordinate of the flow tube, cm
R radius of the flow tube, cm
Re Reynolds number based on cylinder (wire) diameter ($2a$)
u flow velocity, cm/s
$u(z)$ flow velocity dependent on z according to the parabolic flow velocity distribution eq. (1), cm/s
v flow velocity far from cylinder, cm/s
w apparent flow velocity defined by eq. (3), cm/s
z dimensionless radial coordinate of the flow tube, r/R

Greek letter
ν kinematic viscosity, cm^2/s (centistokes)

Subscripts
o bulk value
T total, for radially changing flow velocity in the flow tube

Superscripts
$\bar{}$ average value
$'$ based on average flow velocity

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INTRODUCTION

In several excellent papers on this subject the importance of the kinetics and mechanism of the reaction between CO_2 and alkanolamines has been pointed out sufficiently [see, for example, Kohl and Riesenfeld (1979)]. Although a great number of data have been presented on the reaction between CO_2 and diethanolamine (DEA) (Hikita *et al.*, 1977a; Alvarez-Fuster *et al.*, 1980; Laddha and Danckwerts, 1981,

1982; Barth *et al.*, 1984; Blanc and Demarais, 1984; Blauwhoff *et al.*, 1984; Sada *et al.*, 1985; Tseng *et al.*, 1988) no general agreement on the reaction rate constants exists. However, the zwitterion mechanism proposed originally by Caplow (1968) is uniformly accepted as the reaction mechanism.

Versteeg and van Swaaij (1988a) remarked that for the experimental data obtained from absorption experiments only a relatively small scatter was found. For the data determined with other experimental techniques substantial deviations existed (Hikita *et al.*, 1977a; Barth *et al.*, 1984). Reevaluation of the absorption experiments of Blauwhoff *et al.* (1984) with new, additional data on the combined solubility–diffusivity parameter $m_{N_2O}\sqrt{D_{N_2O}}$ (Versteeg *et al.*, 1987) reduced considerably the gap between the outcome of the experiments from the various techniques (Versteeg and van Swaaij, 1988a).

As already mentioned above the zwitterion mechanism is generally accepted for the description of the reaction between CO_2 and primary and secondary amines:

$$CO_2 + R_1R_2NH \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} R_1R_2NH^+COO^- \quad (1)$$

$$R_1R_2NH^+COO^- + B \xrightarrow{k_b} R_1R_2NCOO^- + BH^+. \quad (2)$$

According to Blauwhoff *et al.* (1984) apart from the amine, water and hydroxyl ions can also contribute to the deprotonation of the zwitterion in aqueous solutions. However, Versteeg and van Swaaij (1988a) observed that it was very difficult to determine the contribution of the hydroxyl ion due to its very low concentration, and they concluded that it could be neglected without a substantial loss of accuracy. The forward rate expression can be derived from the assumption of a pseudo steady state for the zwitterion:

$$R_{CO_2} = \frac{[R_1R_2NH]\,[CO_2]}{\frac{1}{k_2} + \frac{k_{-1}}{k_2 \Sigma k_b [B]}} \quad (3)$$

which leads for an aqueous DEA solution to

$$R_{CO_2} = \frac{[DEA]\,[CO_2]}{\frac{1}{k_2} + \frac{k_{-1}}{k_{H_2O}[H_2O] + k_{DEA}[DEA]}}. \quad (4)$$

From eq. (4) it can be concluded that for the determination of the three reaction rate constants, k_2, k_{H_2O} and k_{DEA}, a substantial variation in the DEA concentration is required.

In this paper additional experimental data are presented on the reaction between CO_2 and aqueous DEA solutions at 298 K. The experimental technique used was similar to Blauwhoff *et al.* (1984) and Versteeg and van Swaaij (1988a). Solubility and diffusivity were determined by means of the CO_2–N_2O analogy (Laddha *et al.*, 1981) and a modified Stokes–Einstein relation (Versteeg and van Swaaij, 1988b), respectively. The DEA concentration was varied between 86 and 8500 mol m^{-3} in order to derive the individual rate constants from the absorption experiments accurately.

RESULTS AND DISCUSSION

For the determination of the physico-chemical constants, solubility and viscosity, one is referred to Versteeg and van Swaaij (1988b). In Table 1 additional data on these constants are presented which were measured in the present study in order to be able to interpret the results of the absorption experiments. A striking result is the substantial increase in the solubility of N_2O at extremely high DEA concentrations: however, a similar effect has been observed for the solubility

Table 1. Solubility of N_2O in aqueous DEA solutions at 298 K

[Amine] (mol m^{-3})	Solubility (mol mol^{-1})	Reference
0	0.600	Versteeg and van Swaaij (1988b)
194	0.585	Present study
201	0.589	Present study
384	0.578	Present study
449	0.595	Sada *et al.* (1977)
523	0.580	Present study
737	0.568	Present study
996	0.588	Sada *et al.* (1977)
1075	0.545	Present study
1397	0.564	Versteeg and van Swaaij (1988b)
1418	0.559	Versteeg and van Swaaij (1988b)
1487	0.550	Present study
1556	0.573	Versteeg and van Swaaij (1988b)
2026	0.565	Sada *et al.* (1977)
2290	0.542	Versteeg and van Swaaij (1988b)
2313	0.556	Sada *et al.* (1977)
2360	0.531	Versteeg and van Swaaij (1988b)
2389	0.553	Versteeg and van Swaaij (1988b)
2848	0.551	Present study
3081	0.535	Sada *et al.* (1977)
3561	0.520	Present study
3669	0.511	Present study
4388	0.497	Present study
5739	0.481	Present study
5852	0.482	Present study
7968	0.404	Present study
8267	0.525	Present study
8553	0.560	Present study
8554	0.543	Present study

of CO_2 in mixed solvents by Takahashi *et al.* (1982).

In Tables 2 and 3 the data for the absorption experiments of the present work and the reevaluated results of Blauwhoff *et al.* (1984) are given, respectively. From Tables 2 and 3 it can be concluded that a good agreement exists between both studies, although the results of Blauwhoff *et al.* (1984) are somewhat higher. The apparent reaction rate constant, k_{app}, was corrected for the reaction of CO_2 with the hydroxyl ions. Blauwhoff *et al.* (1984) showed that for the conditions which occur during the experiments the contribution of the direct hydration of CO_2 to the observed reaction rate is very small for primary and secondary amines. The three reaction rate constants are calculated from the data presented in Tables 2 and 3 by means of an optimization technique and the outcome is presented in Table 4. For DEA concentrations above 6000 mol m^{-3} it was not possible to derive reaction kinetics from the absorption data. It should be noted that in Table 3 the highest concentration reported is 4360 mol m^{-3} as the next concentration studied was above 6000 mol m^{-3}. This can be caused by the substantial decrease in the H_2O concentration for these solutions, and therefore possibly leads to an insufficient solvatation of the alkanolamine which may affect the reaction.

Barth *et al.* (1984) studied the absorption of CO_2 in aqueous DEA solutions for DEA concentrations below 100 mol m^{-3}. From the present results it can be shown that for very low DEA concentrations the reaction rate expression (4) ultimately will reduce to

$$R_{CO_2} \approx \frac{k_2}{k_{-1}} k_{H_2O}[H_2O][DEA][CO_2] \approx 0.095[DEA][CO_2] \quad (5)$$

and from eq. (5) a pseudo-second-order reaction rate constant can be derived which is equal to 0.095 mol m^{-3}. This latter value is in good agreement with the value, 0.110 mol m^{-3}, presented by Barth *et al.* (1984). However, for the experimental conditions studied by Barth *et al.* (1984) the simplification mentioned above is not allowed as the contribution of DEA to the deprotonation of the zwitterion cannot be neglected. Therefore in Fig. 1 the pseudo-first-order reaction rate constants of Barth *et al.* (1984) are compared with the rate constants calculated from Table 4. The work of Hikita *et al.* (1977a) is also included in Fig. 1. From Fig. 1 it can be concluded that there is a good agreement between the results of these studies and that the experimental technique has no influence on the outcome of the calculation of the kinetics from the experiments.

Versteeg and van Swaaij (1988a) suggested that for various alkanolamines a relation exists between k_2 and the basicity of the alkanolamine (pK_a). The previously published values for k_2 by Blauwhoff *et al.* (1984) and Laddha and Danckwerts (1981) deviate substantially from the proposed correlation whereas the new results do not. From the results of the present study it was possible to derive more accurately the value of k_2 and as can be concluded from Fig. 2 this latter value fits extremely well the relation proposed [eq. (6)]:

$$\ln k_2 = pK_a + 16.26 - \left(\frac{T_a}{T}\right) \quad (6)$$

in which $T_a = 7188$ K (Versteeg and van Swaaij, 1988a).

Table 2. Experimental results from present study

[Amine] (mol m^{-3})	[H_2O] (mol m^{-3})	k_{app} (s^{-1})
86	54,850	12
91	54,894	13
97	54,862	14
169	54,520	37
170	54,380	31
201	54,322	49
205	54,301	52
258	54,060	70
314	53,770	101
377	53,440	126
443	53,100	160
484	52,890	174
517	52,710	215
585	52,360	263
616	52,200	274
663	51,960	287
685	51,840	304
709	51,720	357
723	51,650	366
767	51,420	377
809	51,200	457
871	50,880	494
925	50,600	470
1003	50,200	579
2226	43,860	2213
2802	40,600	3878
2832	40,600	3978
2869	40,400	4229
3572	36,800	5678
3653	36,300	5382
3698	36,100	5564
4292	33,000	7060
4318	32,700	5866
4358	32,700	6479

Table 3. Reevaluated results of Blauwhoff *et al.* (1984)

[Amine] (mol m^{-3})	[H_2O] (mol m^{-3})	k_{app} (s^{-1})
393	52,960	145
509	52,600	226
515	52,600	244
542	52,110	217
586	51,940	255
766	51,000	367
833	50,350	483
900	50,600	561
980	50,100	643
993	50,100	674
996	50,100	720
1374	47,820	1008
1731	45,930	1498
1834	44,900	1613
1834	44,900	1655
1874	45,300	1740
1881	44,900	1717
1883	44,800	1717
1889	45,400	2116
1895	44,800	2022
1953	44,800	2004
1956	44,750	1755
1978	45,000	2148
2031	44,700	2282
2033	44,700	2223
2045	44,700	2430
2104	44,300	2025
2164	44,000	2482
2169	44,000	2460
2308	43,100	2913

Table 4. Fitted values of kinetic constants

Reference	k_2 ($m^3\ mol^{-1}\ s^{-1}$)	$k_2 k_{H_2O}/k_{-1}$ ($m^6\ mol^{-2}\ s^{-1}$)	$k_2 k_{Am}/k_{-1}$ ($m^6\ mol^{-2}\ s^{-1}$)
Versteeg and van Swaaij (1988a)	5.79	3.61×10^{-6}	5.34×10^{-4}
Present study	3.24	1.71×10^{-6}	7.07×10^{-4}
Laddha and Danckwerts (1981)	8.59		

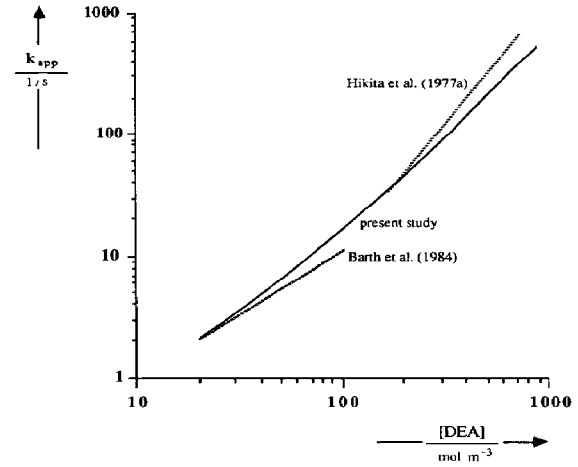

Fig. 1. Comparison between the results of Hikita, Barth and the present study.

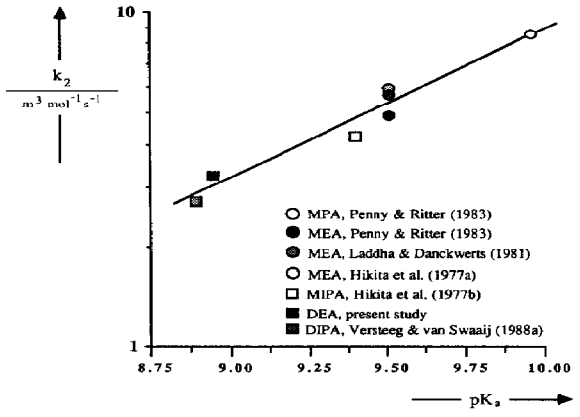

Fig. 2. Brønsted plot for primary and secondary alkanolamines at 298 K.

CONCLUSIONS

In the present study the kinetics between CO_2 and aqueous DEA solutions at 298 K have been studied in order to clarify the remaining discrepancies observed in the open literature (Versteeg and van Swaaij, 1988a). From the results of the present study it can be concluded that the reaction between CO_2 and DEA can be described satisfactorily by the zwitterion mechanism and that all results published can be explained with this mechanism.

The relationship between the second-order rate constant, k_2, of the formation of the zwitterion and the acid-dissociation constant of the alkanolamine as proposed by Versteeg and van Swaaij (1988a) is also valid for DEA.

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NOTATION

Am	amine
B	base
D	diffusivity, $m^2\ s^{-1}$
H_2O	water
k_{-1}	backward first-order reaction rate constant, s^{-1}
k_2	forward second-order reaction rate constant, $m^3\ mol^{-1}\ s^{-1}$
k_b	forward second-order reaction rate constant for base B, $m^3\ mol^{-1}\ s^{-1}$
k_{app}	apparent rate constant, s^{-1}
m	dimensionless solubility
R_{CO_2}	reaction rate, $mol\ m^{-3}\ s^{-1}$
T	temperature, K
T_a	activation temperature, K
[ ]	concentration, $mol\ m^{-3}$

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